A VUV Photoionization Study on the Formation of Primary and Secondary Products in the Reaction of the Phenyl Radical with 1,3-Butadiene under Combustion Relevant Conditions

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Abstract

We studied the reaction of phenyl radicals (C_6H_5) with 1,3-butadiene ($H_2CCHCHCH_2$) exploiting a high temperature chemical reactor under combustion-like conditions (300 Torr, 873 K). The reaction products were probed in a supersonic beam by utilizing tunable vacuum ultraviolet (VUV) radiation from the Advanced Light Source and by recording the photoionization efficiency (PIE) curves at mass-to-charge ratios of m/z = 130 ($C_{10}H_{10}^+$), 116 ($C_9H_8^+$), and 104 ($C_8H_8^+$). Our data suggest that the atomic hydrogen (H), methyl (CH_3), and vinyl (C_2H_3) losses are open with estimated branching ratios of about 86 ± 4 %, 8 ± 2 %, and 6 ± 2 %, respectively. The isomer distributions were probed further by fitting the recorded PIE curves with a linear combination of the PIE curves of individual $C_{10}H_{10}$, C_9H_8, and C_8H_8 isomers. These fits indicate the formation of three $C_{10}H_{10}$ isomers (trans-1,3-butadienylbenzene, 1,4-dihydronaphthalene, 1-methylindene), three C_9H_8 isomers (indene, phenylallene, 1-phenyl-1-methylacetylene), and a C_8H_8 isomer (styrene). A comparison with results from recent crossed molecular beams studies of the 1,3-butadiene – phenyl radical reaction and electronic structure calculations suggests that trans-1,3-butadienylbenzene (130 amu), 1,4-dihydronaphthalene (130 amu), and styrene (104 amu) are *primary* reaction products formed as a consequence of a bimolecular reaction. 1-methylindene (130 amu), indene (116 amu), phenylallene (116 amu), and 1-phenyl-1-methyl-acetylene (116 amu) are *secondary* products synthesized upon reaction of the phenyl radical with three C_4H_6 isomers 1,2-butadiene ($H_2CCCH(CH_3)$), 1-butyne ($HCCC_2H_5$), and 2-butyne (CH_3CCCH_3); these C_4H_6 isomers can be formed from 1,3-butadiene via hydrogen atom assisted isomerization or via thermal rearrangements involving hydrogen shifts in the high temperature chemical reactor.

1. Introduction

In the the last decades, the mechanisms of formation of polycyclic aromatic hydrocarbons (PAHs) have been the focus of extensive studies due to their importance in combustion,[1,2] atmospheric,[3] and interstellar chemistry.[4,5] Combustion and interstellar chemistry models suggest that the phenyl radical in its ground electronic state (C_6H_5, X^2A_1) plays a crucial role in the formation of PAHs,[6,7] especially via its reactions with unsaturated hydrocarbons such as (substituted) acetylenes, olefins, and aromatic molecules.[8-14] Therefore, the reactions of phenyl radicals with unsaturated C3 and C4 hydrocarbons have been studied extensively both experimentally in crossed molecular beams, in high temperature reactors, and computationally. These systems probed the formation of C_9H_x (x = 8, 10)[15-21] and $C_{10}H_x$ (x = 6, 8, 10)[22-27] molecules with indene and naphthalene cores, respectively. Recent crossed molecular beams studies provided compelling evidence that the reactions of the phenyl radical (C_6H_5) with methylacetylene (CH_3CCH) and allene (H_2CCCH_2) lead to the formation of an aromatic indene molecule (C_9H_x).[18,19] Most importantly, bimolecular collisions of phenyl radicals with vinylacetylene ($HCCC_2H_3$) were found to form naphthalene ($C_{10}H_8$) under single collision conditions *without* an entrance barrier to reaction.[23] Likewise, a recent study of the 1,3-butadiene ($H_2CCHCHCH_2$) – phenyl system via crossed molecular beams indicated the *barrier-less* formation of the 1,4-dihydronaphthalene molecule ($C_{10}H_{10}$) together with its trans-1,3-butadienylbenzene ($C_6H_5HCCHCHCH_2$) isomer.[27] These crossed beam studies were able to probe the outcome and hence reaction products of bimolecular reactions without the interference of wall effects, excluding stabilization of reaction intermediates by a third body, and without successive isomerization of the nascent reaction products and/or reactants.

However, in real combustion systems, the reaction mechanisms might be more complicated than those probed under single collision conditions. To account for this, we recently commissioned a high temperature chemical reactor, in which the products of phenyl radical reactions can be probed under combustion-relevant pressures and temperatures.[28] This reactor has been applied very successfully to identify the aromatic indene molecule together with its acyclic isomers (phenylallene, 1-phenyl-1-methylacetylene, and 3-phenyl-1-methylacetylene) in the reactions of phenyl with methylacetylene and allene.[18] Here, we are expanding these studies to probe the products of phenyl radicals reacting with 1,3-butadiene under combustion-like conditions (300 Torr, 873 K) in a high temperature chemical reactor; these findings are compared with the products formed under single collision conditions and predicted computationally.[27]

2. Methods

A resistively heated high temperature 'chemical reactor' interfaced to the molecular beams end station at the Chemical Dynamics Beamline (9.0.2.) of the Advanced Light Source[28] was utilized to study the reaction of the phenyl radical with 1,3-butadiene. Briefly, a continuous beam of phenyl radicals (C_6H_5) was generated *in situ* via pyrolysis of the nitrosobenzene precursor (C_6H_5NO; Aldrich) held at 293 K. The latter was seeded in neat 1,3-butadiene carrier gas (1,3-C_4H_6; Sigma), which was expanded at a pressure of 300 Torr through a 0.1 mm orifice into a resistively heated silicon carbide (SiC) tube at temperatures of about 873 K. The 1,3-butadiene molecules did not only act as a seeding gas, but also as a reactant with the pyrolytically generated phenyl radicals. The residence time of the reactant within the tube was estimated to be at least 26 ± 3 μs. This experimental setup guarantees a detection of the *in situ* generated products within the molecular beam: after passing a 2 mm skimmer located 10 mm downstream from the silicon carbide nozzle, the neutral molecular beam was crossed by quasi continuous tunable VUV radiation from the ALS downstream at the extraction region of a Wiley–McLaren Reflectron Time-of-Flight (Re-TOF) mass spectrometer. The ions of the photoionized molecules were then extracted and collected by a microchannel plate detector in the Re-TOF mode utilizing a multi-channel scaler. The PIE curves of the products were obtained by plotting the integrated ion counts at desired mass-to-charges, m/z, of m/z = 130 ($C_{10}H_{10}^+$), 116 ($C_9H_8^+$), and 104 ($C_8H_8^+$), versus the photoionization energy between 7.60 and 8.80 eV in steps of 0.05 eV. The signal was normalized to the photon flux. Based on known PIE curves of individual $C_{10}H_{10}$, C_9H_8, and C_8H_8 isomers, the recorded PIE curves were then fit via a linear combination of known PIE curves of these isomers to extract the nature of the products formed.

Note that the PIE curves of individual $C_{10}H_{10}$ isomers do not exist in the literature, and, therefore, had to be recorded in separate experiments (Figure 3). Briefly, the PIE curves of five $C_{10}H_{10}$ isomers: 1,2-dihydronaphthalene (TCI, 98%), 1,4-dihydronaphthalene (TCI, 98%), 2-methylindene (TCI, 98%), 1-methylindene (TCI, 98 %), and trans-1,3-butadienylbenzene (TCI, 98 %) were collected in an identical setup as described above, but without the heated silicon carbide nozzle. For each molecule, a continuous beam of the $C_{10}H_{10}$ isomer was generated by passing helium (Airgas, 99.999 %) carrier gas with a pressure of 300 Torr through a home-made stainless steel bubbler, which contained the individual $C_{10}H_{10}$ isomer at 293 K. This gas mixture was expanded through a 0.1 mm orifice into the source chamber before passing a 2 mm skimmer 10 mm downstream to reach the detector chamber. As for the reaction products, the ions of the photoionized molecules were extracted and collected by a microchannel plate detector in the Re-TOF mode. Individual PIE curves were obtained by plotting the integrated ion counts at a particular mass versus the photoionization energy between 7.60 eV and 8.80 eV in steps of 0.05 eV.

3. Results & Discussion

Figure 2 shows a mass spectrum recorded at a heater temperature of 873 K, where product peaks at m/z = 130, 116, and 104, which correspond to the molecular ions $C_{10}H_{10}^+$, $C_9H_8^+$, and $C_8H_8^+$, respectively, can be discerned clearly. Considering the molecular mass of the reactant molecules, i.e. C_6H_5 (77 amu) and C_4H_6 (54 amu), the products are formed via the atomic hydrogen (reaction (1)), methyl radical (reaction (2)), and vinyl radical loss (reaction (3)) pathways.

(1) $C_6H_5 + C_4H_6 \rightarrow C_{10}H_{10} + H$

(2) $C_6H_5 + C_4H_6 \rightarrow C_9H_8 + CH_3$

(3) $C_6H_5 + C_4H_6 \rightarrow C_8H_8 + C_2H_3$

Based on the raw data, peak intensities of the ion counts, and scaled photon absorption cross sections, branching ratios of 86 ± 4 %, 8 ± 2 %, and 6 ± 2 % were estimated for reactions (1) to (3). Subsequently we attempt to fit the recorded PIEs with a linear combination of PIEs of the corresponding isomers to estimate their branching ratios. First, the PIE of m/z = 130 ($C_{10}H_{10}^+$) (Figure 3a) could be fit with a linear combination of three isomers. These are trans-1,3-butadienylbenzene (44 ± 8 %), 1-methylindene (34 ± 10 %), and 1,4-dihydronaphthalene (22 ± 9 %). We would like to stress that up to 9 % of the 1,4-dihydronaphthalene product could be replaced by 2-methylindene without changing the fit. Therefore, the assignment of 2-

methylindene at levels of 9 ± 9 % is tentative; likewise, the potential contributions of the fifth isomer, 1,2-dihydronaphthalene, are marginal (1 ± 1 %). Second, three C_9H_8 isomers were required to reproduce the PIE of m/z = 116 ($C_9H_8^+$) with indene, phenylallene, and 1-phenyl-1-methylacetylene contributing 53 ± 14 %, 27 ± 5 %, and 20 ± 5 %, respectively (Figure 3b). It was not necessary to include any contributions from the 3-phenyl-3-methylacetylene isomer. The fit of the PIE at 104 ($C_8H_8^+$) is not trivial (Figure 3c). This graph could not be reproduced by assuming that the signal only originates from styrene ($C_6H_5C_2H_3$). A closer look at the mass spectra of the calibrated $C_{10}H_{10}$ isomers revealed that the molecular ions of 2-methylindene and 1,4-dihydronaphthalene fragmented to m/z = 104. After accounting for this finding, we could reproduce the PIE of m/z = 104 with two components: styrene (74 ± 12 %) and 1,4-dihydronaphthalene (26 ± 4 %). It is important to note that this fit is not unique, and up to 15 % of the 2-methylindene isomer can be also included without changing the fit. This is due to the limited signal-to-noise of this channel and also the similar photoionization curves of 1,2- and 1,4-dihydronaphthalene.

To rationalize these findings, we explore the potential energy surface (PES) of the phenyl – 1,3-butadiene reaction computed earlier at the G3(CC,MP2)//B3LYP/6-311G** level of theory (Figure 4) and compare the data from the 'chemical reactor' with those obtained under single collision conditions via crossed molecular beam studies.[27] According to the electronic structure calculations, the phenyl radical can add to the C1 or C2 atom of the 1,3-butadiene forming intermediates **i1** and **i2**, respectively. Note that the addition to the C1 position is effectively barrier-less and involves the formation of a van-der-Waals complex and a submerged barrier in the entrance channel. The intermediate **i1** can either undergo cis-trans isomerization to **i3**, isomerize to **i2**, or emit a hydrogen atom yielding trans-1,3-butadienylbenzene (**p1**). On the other hand, **i2** decomposes via vinyl group loss to styrene ($C_6H_5C_2H_3$; C_8H_8). Isomer **i3** can rearrange to a bicyclic structure **i4**, which then decomposes via hydrogen atom loss to form 1,4-dihydrobenzene (**p2**). Based on these considerations, the $C_{10}H_{10}$ isomers trans-1,3-butadienylbenzene (**p1**) and 1,4-dihydrobenzene (**p2**) together with styrene ($C_6H_5C_2H_3$; C_8H_8) must be classified as *primary* reaction products formed in the bimolecular reaction of the phenyl radical with 1,3-butadiene. Note that under single collision conditions at a collision energy of 55 $kJmol^{-1}$, crossed beam experiments established the formation of mainly 1,4-dihydronaphthalene and with smaller fractions trans-1,3-butadienylbenzene as primary reaction products. We would like to stress that the reaction of the phenyl radical with 1,3-butadiene cannot form the $C_{10}H_{10}$ isomer 1-methylindene as well as the three C_9H_8 isomers indene, phenylallene, and 1-phenyl-1-methylacetylene under single collision conditions. Therefore these molecules must be considered as *secondary* reaction products, in the chemical reactor.

We now focus our attention to these *secondary* reaction products and propose potential reaction pathways (Figure 5). Previous electronic structure calculations suggested that 1,3-butadiene can undergo an atomic hydrogen induced isomerization to its less stable 1,2-butadiene, 1-butyne, and 2-butyne isomers.[29] These processes are initiated by an initial addition of atomic hydrogen to 1,3-butadiene to the C1 and/or C2 carbon atom(s) via barriers not exceeding 12 $kJmol^{-1}$ [29] followed by isomerization and hydrogen loss. For instance, 1,3-butadiene and 1,2-butadiene have been monitored in combustion flames of hydrocarbon fuels,[30] and mutual rearrangements between the C_4H_6 isomers were shown to be much faster than their decomposition at flame-relevant temperatures.[31] In our chemical reactor, these hydrogen atoms can be the light byproducts of the reaction of the phenyl radical with 1,3-butadiene yielding the trans-1,3-butadienylbenzene and 1,4-dihydronaphthalene products (Figure 4). Alternatively, all high energy C_4H_6 isomers can be formed easily from 1,3-butadiene through thermal rearrangements involving hydrogen shifts.[32] These isomers – either formed via thermally induced hydrogen migrations or through hydrogen atom induced isomerization - can undergo secondary reactions with the phenyl radical. Here, the phenyl radicals can react with 1,2-butadiene via addition and successive isomerization steps to indene plus methyl, to 1-methylindene plus atomic hydrogen, and to phenylallene plus methyl as demonstrated in previous crossed molecular beam experiments.[24,25] Likewise, phenyl radicals undergo addition to 1- and 2-butyne yielding ultimately phenylallene and 1-phenyl-1-methylacetylene,[26] respectively, via methyl group loss pathways.

4. Summary

A high temperature chemical reactor was utilized to explore the reaction of phenyl radicals (C_6H_5) with 1,3-butadiene ($H_2CCHCHCH_2$) under combustion-like conditions (300 Torr, 873

K). The reaction products were monitored in a supersonic beam by utilizing tunable vacuum ultraviolet (VUV) radiation from the Advanced Light Source and recording the photoionization efficiency (PIE) curves at mass-to-charge ratios of m/z = 130 ($C_{10}H_{10}^+$), 116 ($C_9H_8^+$), and 104 ($C_8H_8^+$). Our data suggest that the atomic hydrogen (H), methyl (CH_3), and vinyl (C_2H_3) losses are open with estimated branching ratios of about 86 ± 4 %, 8 ± 2 %, and 6 ± 2 %, respectively. A detailed fit of the PIE curves and comparison with recent crossed beams and computational works on the phenyl – 1,3-butadiene reaction indicates that trans-1,3-butadienylbenzene (130 amu), 1,4-dihydronaphthalene (130 amu), and styrene (104 amu) are *primary* reaction products (Figure 6). 1-methylindene (130 amu), indene (116 amu), phenylallene (116 amu), and 1-phenyl-1-methylacetylene (116 amu) were identified as *secondary* products synthesized upon reaction of the phenyl radical with the thermodynamically less stable C_4H_6 isomers 1,2-butadiene ($H_2CCCH(CH_3)$), 1-butyne ($HCCC_2H_5$), and 2-butyne (CH_3CCCH_3) as formed from 1,3-butadiene via hydrogen atom assisted isomerization or via thermal rearrangements involving hydrogen shifts. Our studies do not only verify the formation of three combustion-relevant polycyclic aromatic hydrocarbons (indene, 1-methylindene, 1,4-dihydronapthalene) in the chemical reactor, but also underline the necessity to compare experiments in the chemical reactor with those conducted under single collision conditions and with computed potential energy surfaces. This approach ensures to differentiate between primary and higher-order reaction products formed under combustion like conditions in the chemical reactor.

Acknowledgements

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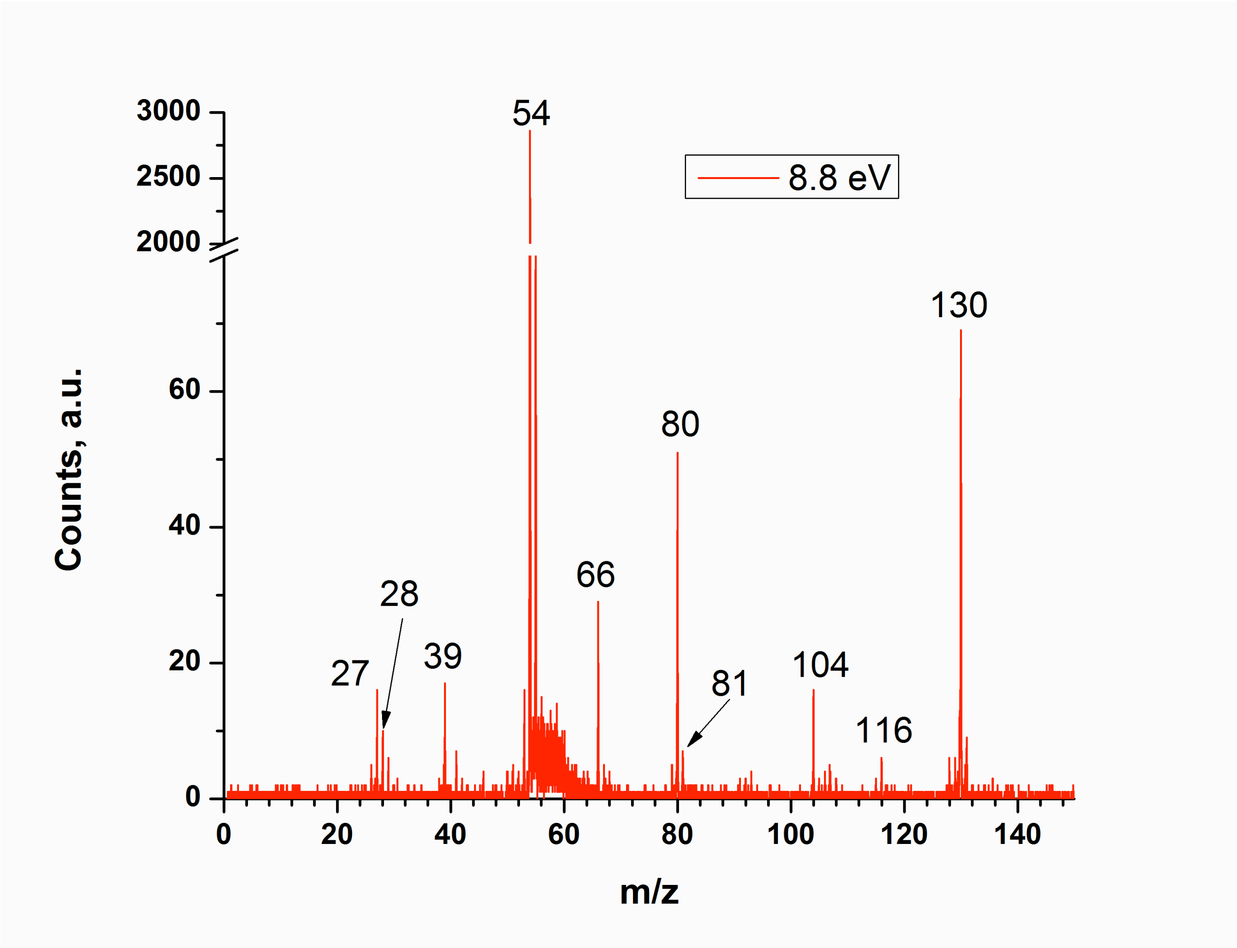

Figure 1. Time of flight mass spectra recorded for an expansion of nitrosobenzene and 1,3 butadiene at a reactor temperature of 873 K, and synchrotron photon energy of 8.8 eV.

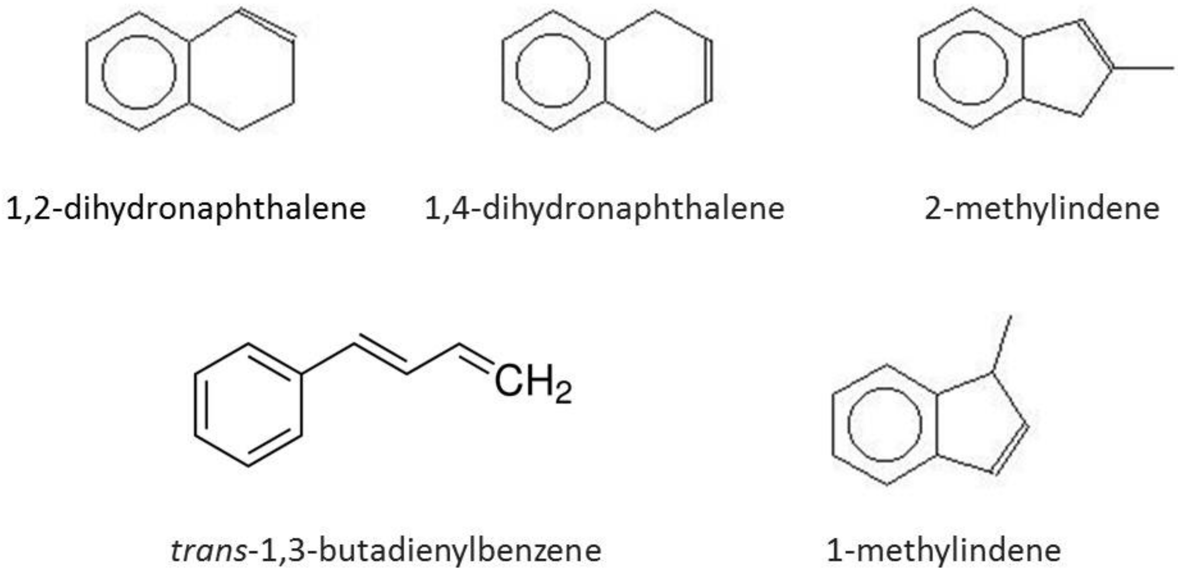

Figure 2: Structures of distinct $C_{10}H_{10}$ isomers potentially formed in the reaction of phenyl radicals with 1,3-butadiene.

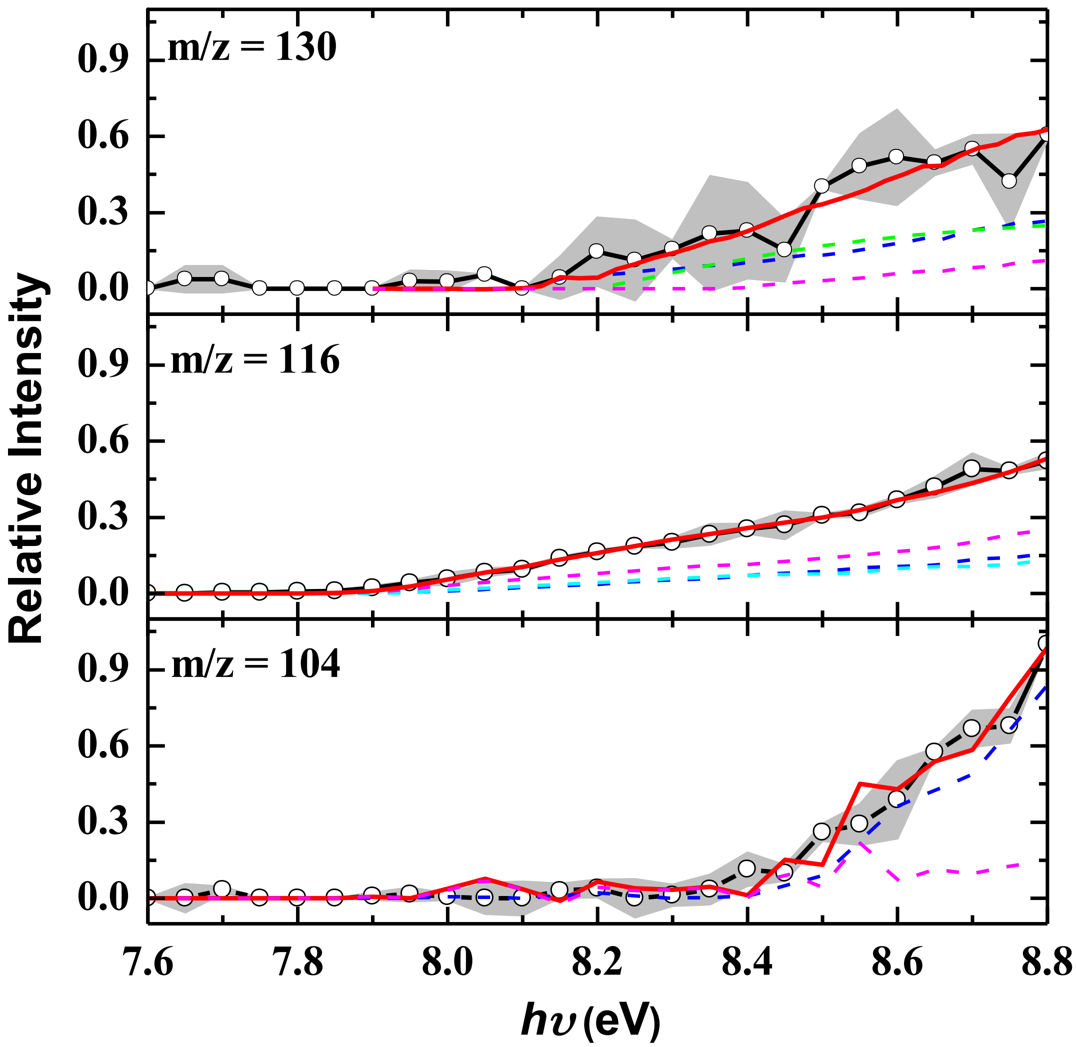

Figure 3: Top: open circles present the PIE obtained at m/z = 130, whereas the red line is the simulation using PIEs of 1,4-dihydronaphthalene (blue), 1-methylindene (cyan), and 1,3-butadienyl-benzene (green). Center: open circles present the PIE obtained at m/z = 116, whereas the red line is the simulation using PIE curves of indene (blue), phenylallene (light blue) and 1-phenyl-1-propyne (magenta). Bottom: open circles present the PIE obtained at m/z = 104, whereas the red line presents the simulation using PIE curves of photoionization fragments of 1,4-dihydronaphathalene (purple) together with the PIE curve of styrene (blue). Experimental errors are defined by the grey curve. The individual PIE curves have been scaled according to their branching ratios.

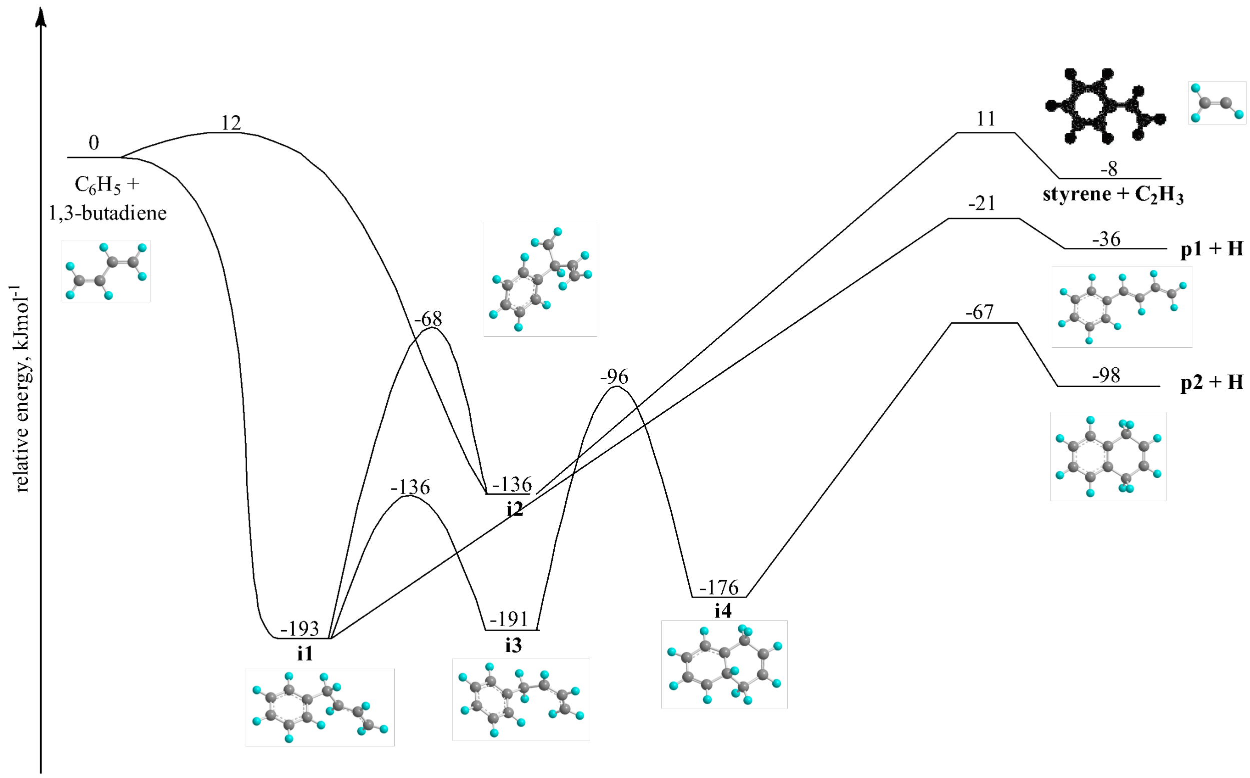

Figure 4: Simplified $C_{10}H_{11}$ potential energy surface (PES) relevant to the reaction of phenyl radicals with 1,3-butadiene computed at the G3(MP2,CC)//B3LYP/6-311G** level of theory. Relative energies are given in kJ mol^{-1}.

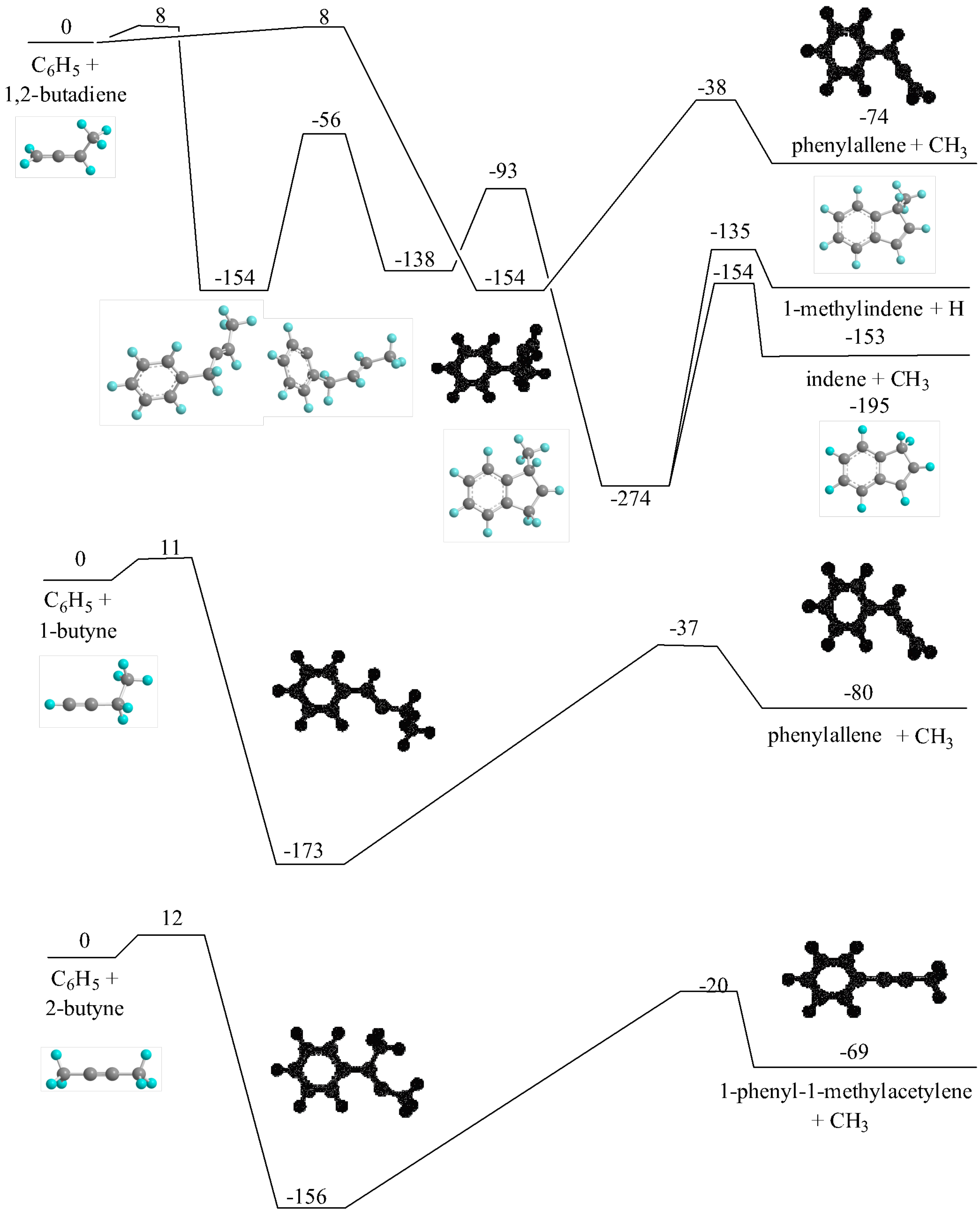

Figure 5: Formation of secondary reaction products via the reactions of phenyl radicals with 1,2-butadiene, 1-butyne, and 2-butyne. Relative energies in kJ mol^{-1} are computed at the G3(MP2,CC)//B3LYP/6-311G** level of theory.

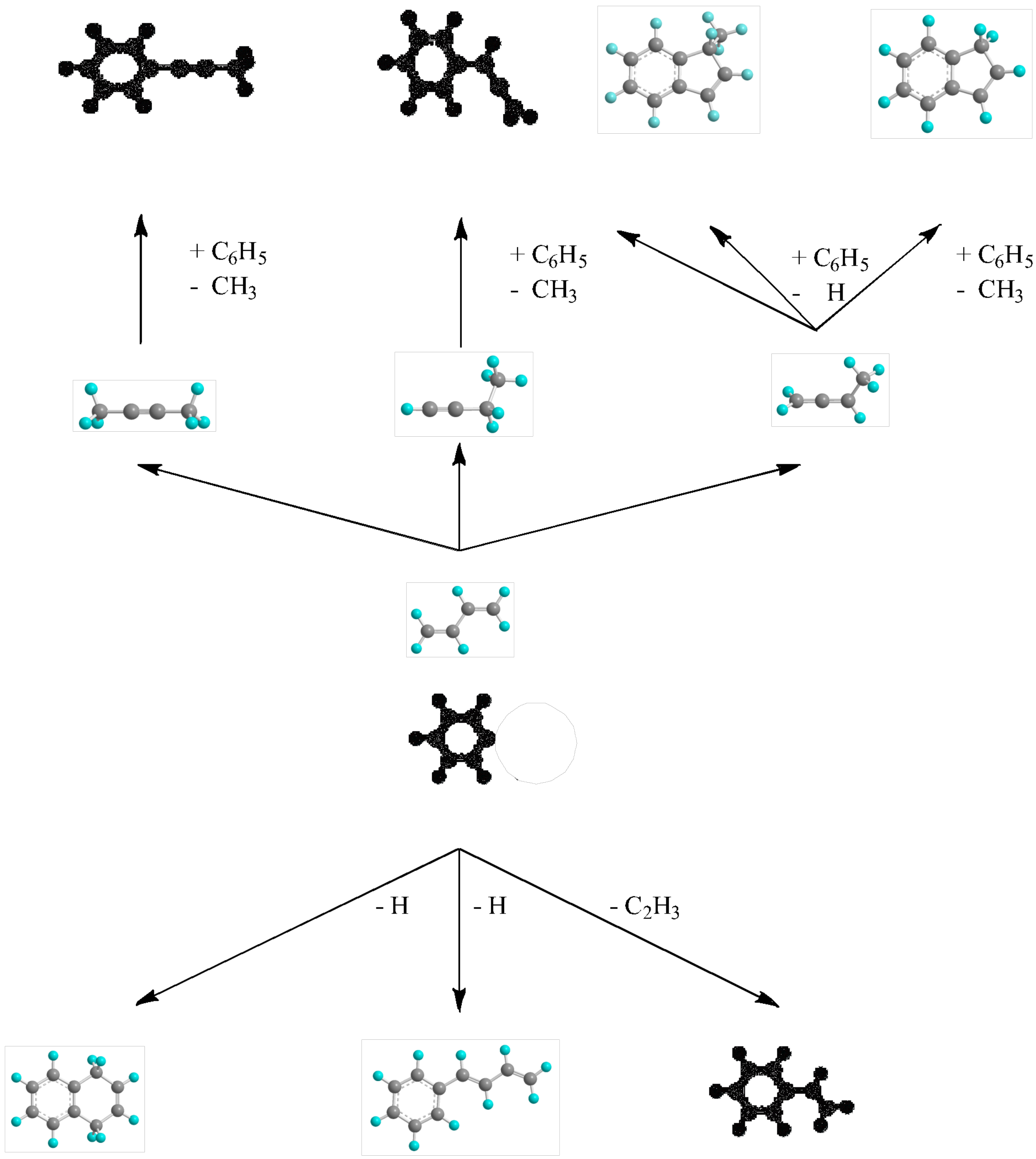

Figure 6: Summary of primary (bottom) and secondary reaction products (upper section) probed in the present experiment.

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